

# Engineering of piezoelectric properties in ferroelectric ceramics and thin films

D. DAMJANOVIC, F. CHU, D. V. TAYLOR, M. DEMARTIN MAEDER, L. SAGALOWICZ, P. DURAN MARTIN, N. SETTER  
Ceramics Laboratory, Materials Department Swiss Federal Institute of Technology - EPFL 1015 Lausanne, Switzerland

The paper discusses different possibilities for controlling piezoelectric properties of ferroelectric materials and devices. The piezoelectric properties engineering can be made on different scales. Tuning of the piezoelectric response by controlling contributions from domain walls displacement is used to illustrate engineering on nanometer scale. Texture control in ferroelectric films and grain size control is discussed as an example of property control on micrometer scale. Finally, engineering on macroscopic (millimeter) scale is illustrated by amplification methods employed in multilayer actuators and different bimorph-type structures as well as by control of electro-mechanical properties in polymer-ceramic composites.

*Key Words: ferroelectric, piezoelectric, thin films, domain-walls*

## Ingeniería de propiedades piezoeléctricas en cerámicas y láminas delgadas ferroeléctricas.

El presente trabajo discute las diferentes posibilidades existentes en el control de las propiedades piezoeléctricas de materiales ferroeléctricos y dispositivos piezoeléctricos. La ingeniería de las propiedades piezoeléctricas se puede llevar a cabo a diferentes niveles. El ajuste de dichas propiedades controlando las contribuciones del desplazamiento de paredes de dominios se usa para ilustrar el diseño a escala nanométrica. El control de la textura en láminas delgadas ferroeléctricas y el control del tamaño de grano serán tratados como un ejemplo del control de propiedades a nivel micrométrico. Por último, la ingeniería de materiales a escala macroscópica (milimétrica) será ilustrada mediante algunos métodos de amplificación empleados en actuadores multicapa y diferentes estructuras de tipo bimorfo, al igual que por métodos de control de las propiedades electro-mecánicas en materiales compuestos polimérico-cerámicos.

*Palabras Clave: ferroelectricidad, piezoelectricidad, láminas delgadas, paredes de dominios*

## 1. INTRODUCTION

Piezoelectric effect in ferroelectric materials is a basis for a large number of devices including pressure, force and vibration sensors, accelerometers, displacement actuators, force generators, transformers, gyroscopes, and high frequency transducers. Piezoelectric materials are among the most promising candidates for active components in the new generation of so-called micro-electro-mechanical systems. In many cases, properties of piezoelectric elements must be tuned to better satisfy requirements of high-performance devices.

Properties of piezoelectric devices may be controlled in several ways, for example by intervening on piezoelectric material itself (by doping, solid solutions, grain-size and microstructure control) (1), by using advantages of composite structures (2), or by adjusting macroscopic structure and design of the piezoelectric element. On the most fundamental level, piezoelectric properties may be engineered by controlling the crystal-lattice (also called intrinsic) response. The best known example is lead zirconate titanate ( $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  or PZT) solid solution, whose electro-mechanical properties may be changed over a wide range of values by varying Zr/Ti ratio. (1,3) Another component of the piezoelectric response in ferroelectric materials can originate from non-lattice (also called extrinsic) contributions. The most commonly considered extrinsic contributions are related to displacements of ferro-

electric domain walls, interphase boundaries and defects (4) The extrinsic part of the piezoelectric effect may be very large, up to 50-70% of the total response (5) The extrinsic component is responsible for effects such as weak-to-moderate field piezoelectric hysteresis, nonlinearity and frequency dependence of the piezoelectric properties (6). Despite the fact that they may increase the magnitude of the piezoelectric coefficient, these extrinsic effects should be reduced in high-precision piezoelectric applications. As will be discussed later, the extrinsic component can be controlled in a number of different ways. In ferroelectric ceramics and thin films engineering of microstructure and texture can be used to control both the intrinsic and the extrinsic response. Finally, the effective piezoelectric properties of devices may be improved by clever device design, and by building macroscopic composite and multilayer structures.

In any given piezoelectric device, it is often necessary to carry out control of its properties on several levels, as illustrated in Figure 1 using the example of multilayer piezoelectric actuators. First, the composition of piezoelectric ceramic is chosen, taking into account several parameters including temperature range of operation, desired piezoelectric displacement, operating voltage, and tolerance of the device to piezoelectric nonlinearity, hysteresis and depoling. These parame-

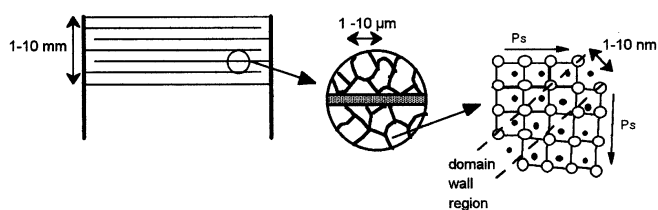


Figure 1 Illustration of three-level engineering essential for optimal design of piezoelectric multilayer actuators. From left to right: multi-layers with internal electrodes; microstructure showing electrode section and individual grains; and domain-walls within grains.

ters can be controlled by chemical modifications and dopants. In this case, modification of the material is made on nanometer level with dopants entering the crystal lattice, segregating into grain-boundaries or diffusing into domain-walls region (7) (see section 2). On the next level, careful control of the microstructure and grain-size of ceramics is essential for tape-casting process as well as for optimal functional properties of the actuator (see section 3). In this case material's engineering is carried out on micrometer scale (typically  $0.1 \mu\text{m}$  to  $10 \mu\text{m}$ ). Finally, the fabrication of multilayers from tape-casted sheets is employed to amplify displacement of the actuator. The piezoelectric element engineering (shape and thickness of active elements, electrical connections, electrodes arrangement etc.) is made in this case on the scale from tens of micrometers to several millimeters.

In this paper different methods of piezoelectric properties engineering in ferroelectric ceramics and thin films are outlined, focusing on microstructural engineering and various means to control domain-wall contributions to the piezoelectric response.

## 2. NANOSCALE EFFECTS

One of the most interesting means to control piezoelectric properties of ferroelectrics is through chemical doping with suitable aliovalent cations. The amount of dopant is usually a fraction to few atomic percent. The best known examples are acceptor and donor doped PZT ceramics. In acceptor doped or "hard" PZT, domain-walls are pinned (immobilized) by defects and are difficult to move by an external field (7). "Hard" PZT exhibit a lower hysteresis and are more difficult to depolarize than "soft" PZT, which are obtained by donor doping. Despite the fact that PZT materials have been used and studied for nearly fifty years, the mechanism which render donor-doped PZT piezoelectrically "soft" (large piezoelectric coefficient, large hysteresis and nonlinearity) are presently not understood. On the other hand, it is now well documented (7,8) that the mechanism of piezoelectric "hardening" in acceptor (usually Fe) doped materials is related to alignment of  $\text{Fe}_{\text{Ti}}$ -VO dipole pairs along polarization vector. Displacement of domain-walls of those domains that contain defect dipoles requires not only switching of the ferroelectric polarization but also reorientation of defect dipoles. This reorientation takes place through migration of the oxygen vacancy. The energy required for domain-wall displacement is thus increased and domain-walls are said to be clamped or pinned. This and related mechanisms have been studied in detail by several groups

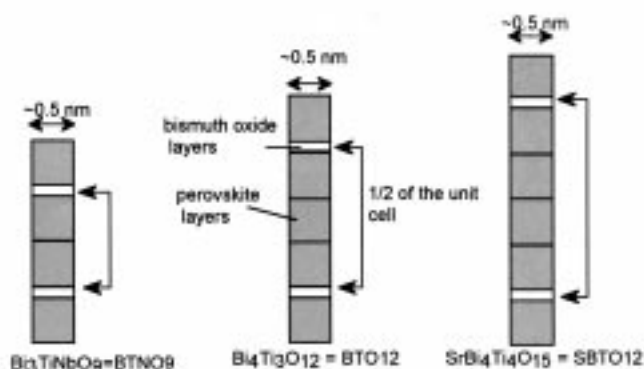


Figure 2 Schematic representation of selected bismuth-titanate based Aurivillius phases. The illustration shows basic building blocks of each compound.

(7,8). Another mechanism that leads to immobilization or pinning of domain-walls is caused by migration of free charges into domain-wall region that is electrically charged. If these mobile charges are trapped in deep levels in the wall region, domain wall becomes more difficult to move (9). It should be pointed out that whereas general ideas of domain-wall pinning mechanisms have been in some cases worked out, the exact details and quantitative understanding of underlying microscopic processes are not well understood. On experimental level, direct evidence of domain-wall pinning and dynamic domain-wall contributions to the electro-mechanical properties are also scarce (10).

There are relatively few studies on piezoelectric properties control in other materials than PZT. In this section we present some recent results obtained on bismuth titanate family of Aurivillius structures. Some members of this family are important high temperature piezoelectrics and others have been intensively studied for non-volatile ferroelectric memories. Bismuth-titanate based Aurivillius structures consist of alternating perovskite and bismuth oxide layers. The number of perovskite-like units which are separated by bismuth oxide layers varies for different structures, as shown in Figure 2.

Figure 3 shows piezoelectric nonlinearity as a function of Nb concentration in Nb doped  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BTO12). Clearly, the nonlinearity (and hysteresis) can be completely suppressed by large enough concentration of Nb. It is interesting that role of donor dopant in BTO12 is opposite to that in PZT. In PZT, Nb softens the piezoelectric response, increasing hysteresis and nonlinearity. In BTO12, hysteresis first becomes larger as Nb is added but then drops rapidly as amount of Nb is increased. Nb appears to be completely soluble in BTO12 up to the largest concentration used, so that effects of a second phase can be excluded. The following hypotheses may be proposed to explain the effect of Nb concentration on the reduction of piezoelectric hysteresis and nonlinearity in BTO12. First, when added in large amounts, Nb might suppress monoclinic distortion of BTO12. It is known that in orthorhombic  $\text{Sr}_4\text{Bi}_4\text{TiO}_{15}$  (SBTO15) the piezoelectric hysteresis and nonlinearity are absent, probably as a consequence of a particular sequence of ferroelectric and ferroelastic phase transitions, which in SBTO15 material do not appear to take place simultaneously (11). If, above some critical concentration of Nb, doped BTO12 becomes orthorhombic, a behavior analogous to that in SBTO15 is not impossible. Unfortunately, monoclinic distortion of BTO12 is very small and difficult to detect. Second, Nb decreases grain size of BTO12 and can affect domain wall con-

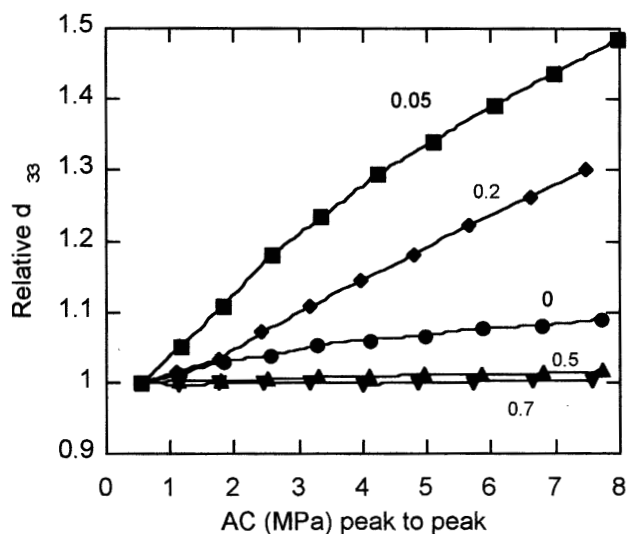


Figure 3 The relative direct longitudinal piezoelectric  $d_{33}$  coefficient in Nb-doped  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  as a function of the driving pressure strength. Numbers represent the concentration of Nb in atomic percent.

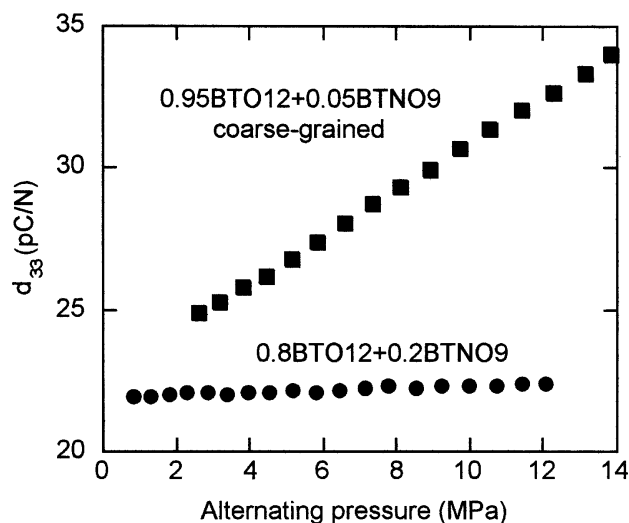


Figure 4 The direct longitudinal piezoelectric  $d_{33}$  coefficient in two compositions of  $(1-x)\text{BTO}_{12}+x\text{BTNO}_9$  solid solution as a function of driving pressure strength.

tribution to the piezoelectric properties by changing configuration and density of domain walls (see Section 3). Third, charges introduced in the material by donor dopant may diffuse into domain-walls region and pin domain walls [9]. Fourth, defect structure in complex ferroelectrics such as BTO12 may be different from that in simple perovskites, so that Nb may not have the same role in BTO12 as in PZT. Fifth, there is experimental evidence (12) that at room temperature the conductivity in BTO12 is controlled by grain boundaries. Doping with Nb reduces conductivity of BTO12, reduces grain size and, consequently, increases grain boundary area. If mobile charges get trapped in low-conductivity grain-boundary region, they could serve as pinning centers for domain-walls. Finally, there is evidence that a density of structural faults in Nb-doped BTO12 increases with Nb concentration. These faults could increase internal stress and immobilize domain walls.

Another way to obtain interesting piezoelectric properties in bismuth titanate family is by making solid solution of two phases (13). Figure 4 shows piezoelectric nonlinearity in two solid solutions of BTO12 and  $\text{Bi}_3\text{TiNbO}_9$  (BTNO9), one with relatively small amount (5%) and other with a large amount (20%) of BTNO9. A strong nonlinearity in  $0.95\text{BTO}_{12}+0.05\text{BTNO}_9$  is accompanied with strong piezoelectric hysteresis (see Figure 7 below). In  $0.8\text{BTO}_{12}+0.2\text{BTNO}_9$ , which exhibits a weak nonlinearity, piezoelectric hysteresis is absent. Again, there are several possible origins of this behavior. An intriguing possibility is suggested by the study of the two materials using transmission electron microscopy (TEM). As presented in Figure 5, TEM observations show that  $0.95\text{BTO}_{12}+0.05\text{BTNO}_9$  forms a complete solid solution of two phases so that crystal structure consists of regular and uniform layers of BTO12 modified by BTNO9. This material exhibits a low density of structural faults. In  $0.8\text{BTO}_{12}+0.2\text{BTNO}_9$ , density of stacking faults is higher. The stacking faults have been identified as intergrowth layers of BTNO9 which, once the solubility limit is reached, is not dissolved in BTO12, and which breaks the regular sequence of modified BTO12 layers. The intergrowth layers are expected to create significant internal stress in the structure, which can make displacement of

domain walls more difficult. The internal stress would thus have the similar role as internal electric field. Other possibilities for reduction of domain wall contributions to piezoelectric effect in  $0.8\text{BTO}_{12}-0.2\text{BTNO}_9$  are related to the presence of large concentration of Nb, and include mechanisms similar to those observed in Nb-doped BTO12, discussed above.

### 3. MICROSTRUCTURAL ENGINEERING

In this section the grain-size effects in ceramics, averaging of ceramics properties over contributions from individual grains and texture effects in thin films, are discussed as examples of control of extrinsic and intrinsic piezoelectric properties at microscopic level.

#### 3.1 Apparent grain size effects

##### 3.1.1. PZT CERAMICS

Effects of grain-size on properties of ferroelectric ceramics have been a subject of many studies (14). Perhaps the best known example is the grain size dependence of dielectric permittivity in barium titanate ( $\text{BaTiO}_3$  or BT) (15). There are comparatively fewer systematic studies of the grain size effects on piezoelectric properties. While the correlation between grain-size and piezoelectric properties has been well established experimentally in ferroelectric ceramics, the mechanisms by which grain size controls piezoelectric response in multi-oxide systems are presently not well understood. The main reason for this is the difficulty to separate the effects of several other parameters that may change simultaneously with the grain-size. This is well illustrated on the example of apparent grain-size dependence of piezoelectric coefficients in  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  ceramics doped with 2 % Nb and prepared by classical mixed oxide method. Despite the scattering in data, a clear trend in piezoelectric coefficients vs. grain size relationship is observed. Careful examination of ceramics

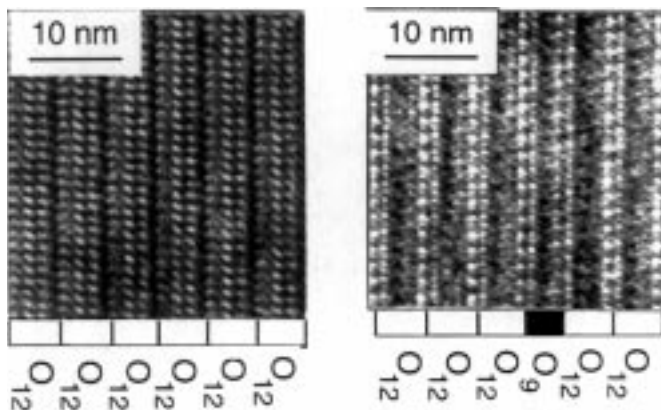


Figure 5 TEM image of layered structure of 0.95BTO12+0.05BTNO9 and 0.80BTO12+0.20BTNO9 solid solutions. Intergrowth layers are seen in 0.80BTO12+0.20BTNO9 where the limit of complete solubility of the two phases might have been reached.

using X-ray diffraction, temperature dependence of elastic modulus and chemical analysis with TEM reveal that the dependence in grain size is accompanied with changes in crystallographic structure of ceramics and chemical homogeneity within grains. Ceramics with fine grains ( $\sim 1 \mu\text{m}$ ) exhibit a mixture of tetragonal (Ti rich) and rhombohedral (Zr rich) phases, and show a large variation of Ti/Zr ratio within grains. Large grain ceramics ( $\sim 8 \mu\text{m}$ ) exhibit tetragonal structure and much less variation in Ti/Zr ratio within grains. Lower degree of homogeneity in fine-grained samples is expected since low temperature and a short sintering time limit diffusion of ions. An attempt to thermally anneal fine-grained ceramics and improve homogeneity led to grain growth. Thus, grain growth on one side and structural and chemical homogenization on other side are found to be linked, making difficult interpretation of the principal and secondary mechanisms responsible for the apparent grain size dependence of piezoelectric properties. It is interesting to note that the study of grain-size dependence of electro-mechanical properties is more complicated in PZT than in BT which contains only one cation on B-site and grain size can be more easily controlled independently of other parameters. It should be mentioned that the true grain size dependence of piezoelectric properties in PZT may be established by studying ceramics prepared by chemical methods which, at least in principle, may lead to a better chemical homogeneity even in fine-grained materials.

### 3.1.2. BISMUTH TITANATE BASED CERAMICS

One important disadvantage of ferroelectric ceramics for high precision sensor and actuator applications is the piezoelectric hysteresis between driving electric field (or pressure) and piezoelectric strain (or charge). In most cases the origin of the hysteresis is in the displacement of ferroelectric domain walls [6]. The best-known method to immobilize domain walls and reduce hysteresis is to pin or clamp the walls with suitable defects, as discussed in section 2. On the other hand, it is reasonable to expect that microstructure can also affect domain-wall contributions to electro-mechanical properties. First, it is well known from the studies made on barium titanate that the domain-wall structure and domain-wall density

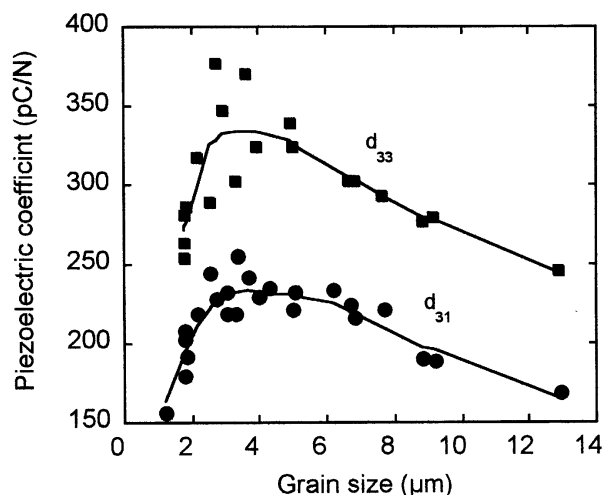


Figure 6 Longitudinal  $d_{33}$  and transverse  $d_{31}$  piezoelectric coefficients in  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  ceramics doped with 2%Nb. Ceramics were prepared by mixed-oxide method.

are very different in fine and coarse-grained ceramics (16, 17). Clearly, domain-wall contributions to electromechanical properties coming from different types and density of domain walls may not be the same. Second, some theoretical studies indicate that domain walls of narrow domains (usually found in fine-grained materials) are more difficult to move than domain walls of wide domains (found in coarse-grained materials) (18). Third, specific domain-wall structure of fine grains may lead to high internal stresses in ceramics (19). A large internal stress may affect intrinsic (lattice) properties of the material as well as displacement of ferroelastic-ferroelectric domain walls. In the latter case internal stress can have a similar role as internal electric field. These arguments were used as a possible explanation of grain size effects on piezoelectric properties in barium titanate ceramics (20).

In this section we discuss recent results on grain-size effects on piezoelectric hysteresis and nonlinearity in bismuth titanate based Aurvillius phases. In these layer-structured ferroelectrics domain wall configuration may be more complex (21) than in tetragonal and rhombohedral perovskite materials so that simple extrapolation of results observed in PZT and BT to bismuth titanate family is not always justified. shows piezoelectric hysteresis for solid solution of  $0.95\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and  $0.05\text{BiTiNbO}_9$ , for a coarse-grained and a fine-grained material. It is evident (taking into account difference in piezoelectric coefficient) that the piezoelectric hysteresis is much weaker in the fine-grained material. The reduction in hysteresis is accompanied with the reduction in piezoelectric nonlinearity (13). The weaker nonlinearity, lower hysteresis and piezoelectric coefficient in fine-grained 0.95BTO12+0.05BNTNO9, suggest (6) weaker domain-wall contributions to the piezoelectric properties than in coarse-grained material. As in the case of barium titanate, one can speculate that the reduction in domain-wall contributions is related to internal stresses or smaller width of domain walls in fine-grained material. Another possibility for reduction in domain wall contributions would be that fine-grained ceramics possess a higher density of stacking faults. The mechanism would thus be similar to that discussed in section 1 for 0.8BTO12+0.2BNT. The origin of stacking faults in



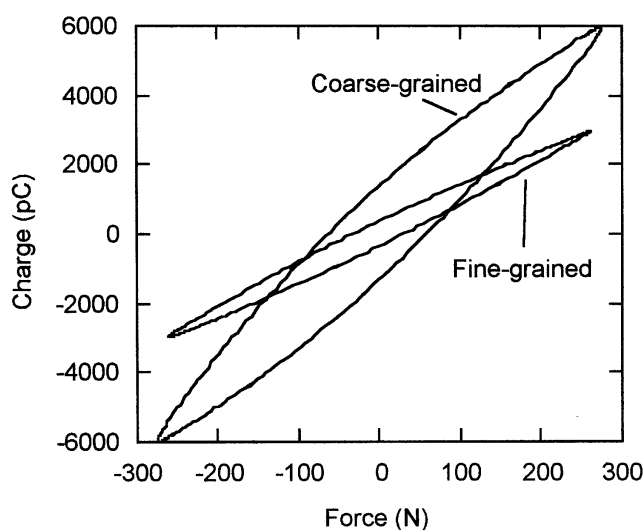


Figure 7 Piezoelectric hysteresis for coarse and fine-grained samples of 0.95BTO12+0.05BTNO9 solid solution.

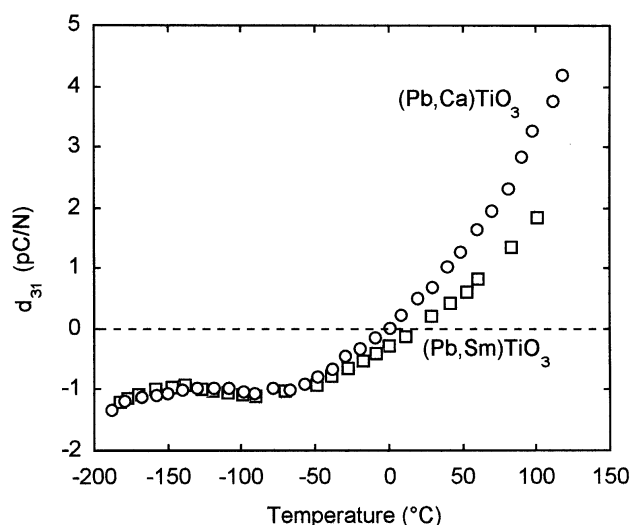


Figure 8 Temperature dependence of transverse piezoelectric  $d_{31}$  coefficient of  $(\text{Pb,Ca})\text{TiO}_3$  and  $(\text{Pb,Sm})\text{TiO}_3$  ceramics.

fine-grained 0.95BTO12-0.05BNT09 could be in low sintering temperature and short sintering time, which may not be sufficient for a complete solubility of two phases. Note that, if stacking-faults were indeed responsible mechanism for suppressed domain wall contributions to piezoelectric properties, the grain-size would again be a secondary effect.

### 3.2 Averaging of piezoelectric properties in ceramics

Global properties of a ferroelectric ceramic are average values of properties of (usually) randomly oriented crystallites (grains) which form ceramic. In ferroelectric ceramics, grains are divided into ferroelectric domains, which can also have different orientations. This averaging of properties of all grains and domains can lead to unusual but very useful piezoelectric properties, as shown on the following example. An interesting feature of modified lead titanate ( $\text{PbTiO}_3$  or PT) ceramics is a large anisotropy in piezoelectric coefficients (a large ( $\sim 50$  pC/N) longitudinal  $d_{33}$  and a small transverse  $d_{31}$  coefficient) (22). In most ferroelectric materials the  $d_{33}/d_{31}$  ratio is 2-3 whereas in modified lead titanate ceramics it may become many times higher. Materials with a small  $d_{31}$  are useful in applications where high directivity and low lateral coupling to longitudinal mode are needed.

Several attempts to model piezoelectric response of modified lead titanate ceramics have shown that the origin of the piezoelectric anisotropy in PT-based ceramics is in averaging of the single crystal coefficients over all possible orientations of grains and domains (23, 24). The effect of averaging can be seen by considering the simplest formula (24) which relate effective (averaged) coefficients of ceramics and single crystals:

$$d_{31} = (1 + \cos \theta) [4d_{31}^{\text{sc}} + (d_{33}^{\text{sc}} - d_{31}^{\text{sc}} - d_{13}^{\text{sc}}) \sin^2 \theta] / 8 \quad [1]$$

$$d_{33} = (1 + \cos \theta) [2d_{33}^{\text{sc}} - (d_{33}^{\text{sc}} - d_{31}^{\text{sc}} - d_{13}^{\text{sc}}) \sin^2 \theta] / 4 \quad [2]$$

where  $d_{ij}$  and  $d_{ij}^{\text{sc}}$  denote ceramic and single-crystal coefficients, respectively. In this simple model ceramic grains are assumed to be single-domain crystallites.  $\theta$  is then the maximum angle between direction of the polarizing electric field and the spontaneous polarization vector of the crystallites. Furthermore, single-crystal piezoelectric coefficients may be related by phenomenological theory to dielectric permittivity, spontaneous polarization and electrostrictive coefficients (25). Calculations show that particular values of these properties and their temperature dependencies lead to a small  $d_{31}$  and a relatively large  $d_{33}$  in many modified lead titanate compositions over a wide range of temperatures. It is seen from equation [1] that, under right conditions,  $d_{31}$  can become zero or even positive. This has been indeed observed experimentally, as shown in Figure 8 for  $(\text{Pb,Sm})(\text{Mn,Ti})\text{O}_3$  and  $(\text{Pb,Ca})\text{TiO}_3$  ceramics (26). A detailed discussion of microstructural effects on the piezoelectric anisotropy in modified lead titanate ceramics can be found in Ref. (27).

### 3.3 Effects of crystallographic orientation in PZT thin films

Ferroelectric thin films are very interesting from the aspect of control of electro-mechanical properties. Besides compositional and microstructural effects already mentioned for bulk materials, thin films offer additional possibilities to engineer piezoelectric properties. For example, it is well known that variations in thickness, crystallographic orientation or texture, and substrate properties affect properties of ferroelectric films. Take as an example the most widely used ferroelectric piezoelectric, PZT. Because single crystals of PZT are not available, crystal orientation effects can be studied only on thin films, which can be readily grown in different orientations, either as polycrystalline or epitaxial (28). Furthermore, not only does effective intrinsic piezoelectric coefficient of films change with orientation, but domain-walls configuration and their contributions to the properties also depend on film orientation. This is illustrated below on example of sol-gel derived rhombohedral thin films (29).

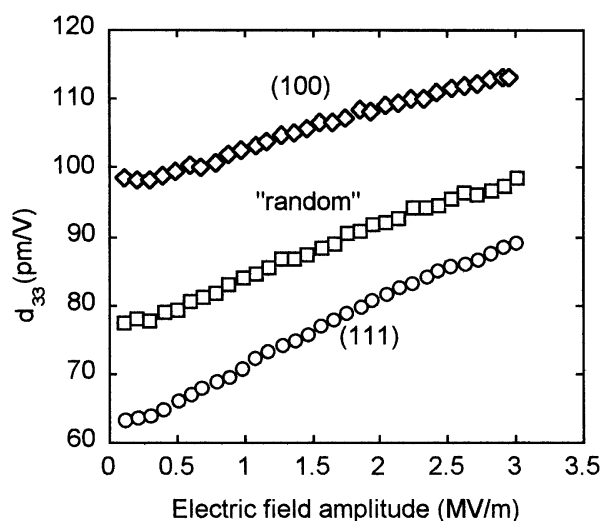


Figure 9 Effective longitudinal  $d_{33}$  coefficient for three orientations of  $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$  thin films as a function of driving electric-field amplitude.

Piezoelectric effect in PZT single crystals has been recently calculated as a function of crystal orientation [30]. The calculations showed that the largest longitudinal  $d_{33}$  piezoelectric coefficient should be observed in rhombohedral (Zr rich) crystals near the morphotropic phase boundary, along (100) direction. It is interesting that this direction is not the direction of the ferroelectric polarization, which is oriented along (111) direction of the rhombohedral unit cell. shows the effective  $d_{33}$  longitudinal piezoelectric coefficient measured in rhombohedral  $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$  films with different orientation. As predicted by calculations, (100) films have significantly higher piezoelectric coefficient than other orientations. From the application point of view, it is significant that (100) film also shows the weakest nonlinearity. The weak nonlinearity is a consequence of particular configuration of ferroelectric domains for this orientation. As in the case of (111) oriented tetragonal films, displacement of non-180° domain walls in (001) oriented rhombohedral films will not change dimensions of the film along direction perpendicular to the film plane, and will thus not directly contribute to the longitudinal piezoelectric effect.

This example illustrates how control of film orientation affects both intrinsic (through crystal anisotropy) and extrinsic (through domain wall contribution) components of piezoelectric effect in PZT thin films.

#### 4. LARGE SCALE ENGINEERING

Several examples of piezoelectric engineering on macroscopic scale (tens of microns to one millimeter) are illustrated in. Figure 10. One of the most interesting and elegant examples is a ceramic-polymer composite. The macroscopic engineering in piezoelectric composites is based on symmetry, connectivity, shape and the volume ratio of the two phases (2). The soft polymer matrix has multiple roles. It reduces cross talk between elements in a transducer array by dampening acoustic waves propagating in lateral directions. By the same mechanism (reduction of the effective lateral piezoelectric coefficient), the polymer matrix increases hydrostatic piezoelectric

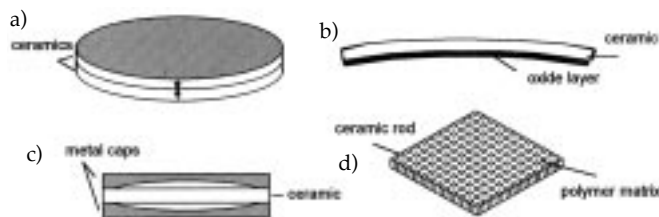


Figure 10 Examples of engineering of piezoelectric properties on macroscopic scale: a) piezoelectric disk bimorph, b) Rainbow ceramic, c) Moonie flextensimas actuator, and d) piezoelectric polymer-ceramic composite.

coefficient in hydrophones. Finally, by reducing density and increasing elastic compliance of the composite, the soft polymer matrix improves acoustical impedance matching between transducer and water (in hydrophones) or biological tissue (in medical imaging transducers).

Next example demonstrates how large-scale engineering of piezoelectric properties can be used to amplify displacement of piezoelectric elements. Amplification may be achieved by classical multilayer structures and by several types of bimorph structures and so-called flextensional devices. A recent new concept called RAINBOW (Reduced and Internally Biased Oxide Wafer) illustrates well the idea (31). A piezoelectric disk is placed in contact with a block of carbon and heated. The side of the ceramic disk that is in contact with carbon will get chemically reduced creating a relatively thick metallic layer. On cooling, the disk bends due to difference in thermal expansion between metallic layer and ceramic. When partially reduced and polarized ceramic is driven with electrical field applied on major faces, disk changes dimensions due to the piezoelectric effect. In thin disks with large diameter, change in lateral dimension is very high. Since the reduced layer is piezoelectrically passive, the whole structure must further bend under the driving field, giving a large displacement (tens of microns) in the direction parallel to the field. Disadvantage of RAINBOWs is in difficulties to partially reduce ceramics in a reproducible way.

Amplification of the longitudinal displacement by lateral bending can be induced in a number of ways. For example, two piezoelectric disks or beams glued to each other and poled in opposite directions will also lead to bending of the "sandwich" structures when driven by an electric field. Because of their geometry, disk benders are expected to be more robust and to generate larger forces than beam-type bimorphs. It is certain that in future we shall see many other designs based on this simple concept. Similar idea for displacement amplification is used in metal-ceramic moonie structures, (32). Besides questions associated with the choice of two materials used to build a bimorph, their relative dimensions and shape, one of the most important material engineering problems to solve is stability of the interface between two materials with different piezoelectric properties (one can be passive).

#### 5. CONCLUSIONS

Engineering of piezoelectric properties in ferroelectric materials presents many challenges both on practical and fundamental level. Whereas control of piezoelectric properties can be achieved and materials with useful properties can be engineered, understanding of underlying processes is in many cases inadequate. Further development of improved piezoelectric

lectric materials will depend on progress in both experimental and theoretical studies of mechanisms that control piezoelectric behavior.

## ACKNOWLEDGMENTS

This work was financially supported by The Swiss Federal Office for Education and Science (OFES) in the framework of the Brite-Euram Project "RANNTAC" (OFES Contract No. 97.0515-2).

## 6. REFERENCES

- 1 B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*. New York: Academic, 1971.
- 2 W. A. Smith, "The role of piezocomposites in ultrasonic transducers," *Proceedings of 1989 IEEE Ultrasonics Symposium*, p. 755-766 (1989).
- 3 M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, "Thermodynamic theory of the lead zirconate-titanate solid solution system, Part V: Theoretical calculations," *Ferroelectrics*, **99**, 63-86, (1989).
- 4 L. E. Cross, "Ferroelectric Ceramics: Tailoring Properties for Specific Applications," in *Ferroelectric Ceramics*, N. Setter and E. L. Colla, Eds. Basel: Birkhäuser, 1993, 1-86.
- 5 E. I. Bondarenko, V. Y. Topolov, and A. V. Turik, "The role of 90° domain wall displacements in forming physical properties of perovskite ferroelectric ceramics," *Ferroelectr. Lett.*, **13**, 13, (1991).
- 6 D. Damjanovic, "Stress and frequency dependence of the direct piezoelectric effect in ferroelectric ceramics," *J. Appl. Phys.*, **82**, 1788-1797, (1997).
- 7 K. Carl and K. H. Haerdtl, "Electrical after-effects in  $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$  ceramics," *Ferroelectrics*, **17**, 473-486, (1978).
- 8 W. L. Warren, K. Vanheusden, D. Dimos, G. E. Pike, and B. A. Tuttle, "Oxygen Vacancy Motion in Perovskite Oxides," *J. Am. Ceram. Soc.*, **79**, 536-38, (1996).
- 9 H. N. Al-Shareef, D. Dimos, W. L. Warren, and B. A. Tuttle, "A model for optical and electrical polarization fatigue in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ," *Integrated Ferroelectrics*, **15**, 53-67, (1997).
- 10 O. A. Tikhomirov, "Vibrations of domain walls in ac field and the low frequency permittivity of ferroelectrics," *Ferroelectrics*, vol. 190, pp. 37-42, 1997.
- 11 I. M. Reaney and D. Damjanovic, "Crystal structure and domain-wall contributions to the piezoelectric properties of strontium bismuth titanate ceramics," *J. Appl. Phys.*, **80**, 4223-4225, (1996).
- 12 P. Duran-Martin, C. Voisard, and D. Damjanovic, "Study and control of the conductivity of Nb-doped  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  for high temperature piezoelectric applications," *Bol. Soc. Esp. Ceram. Vid.*, **38**, 6, 582-586 (1999).
- 13 F. Chu, D. Damjanovic, and N. Setter, "An investigation of dielectric and piezoelectric properties of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}+\text{Bi}_3\text{TiNbO}_9$  ceramics," *Proceedings of Fourth Euroceramics Vol. 5*, Eds. Gusmano G. and Traversa E., Gruppo Editoriale Faenza Editrice.Faenza, 1995.
- 14 C. A. Randall, N. Kim, J. P. Kucera, W. Cao, and T. R. Shrout, "Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics," *J. Am. Ceram. Soc.*, **81**, 677-88, (1998).
- 15 M. H. Frey and D. A. Payne, "Grain-size effect on structure and phase transformations for barium titanate," *Phys. Rev. B*, **54**, 3158-3168, (1996).
- 16 G. Arlt, "Microstructure and domain effects in ferroelectric ceramics," *Ferroelectrics*, **91**, 3-7, (1989).
- 17 G. Arlt, D. Hennings, and G. de With, "Dielectric properties of fine-grained barium titanate ceramics," *J. Appl. Phys.*, **58**, 1619-1625, (1985).
- 18 G. Arlt and N. A. Pertsev, "Force constant and effective mass of 90° domain walls in ferroelectric ceramics," *J. Appl. Physics*, **70**, 2283-2289, (1991).
- 19 W. R. Buessem, L. E. Cross, and A. K. Goswami, "Phenomenological theory of high permittivity in fine-grained barium titanate," *J. Am. Ceram. Soc.*, **49**, 33-36, (1966).
- 20 M. Demartin and D. Damjanovic, "Dependence of the direct piezoelectric effect in coarse and fine grain barium titanate ceramics on dynamic and static pressure," *Appl. Phys. Lett.*, **68**, 3046-3048, (1996).
- 21 S. E. Cummins and L. E. Cross, "Electrical and optical properties of ferroelectric  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  single crystals," *J. Appl. Phys.*, **39**, 2268-2274, (1968).
- 22 H. Takeuchi, S. Jyomura, E. Yamamoto, and Y. Ito, "Electromechanical properties of  $(\text{Pb},\text{Ln})(\text{Ti},\text{Mn})\text{O}_3$  ceramics (Ln=rare earths)," *J. Acoust. Soc. Am.*, **72**, 1114, (1982).
- 23 A. V. Turik, E. G. Fesenko, V. G. Gavrilatchenko, and G. I. Khasabova, "Anisotropy of the dielectric and piezoelectric properties of lead titanate," *Sov. Phys. Crystallogr.*, **19**, 677-678, (1975).
- 24 A. V. Turik and V. Y. Topolov, "Ferroelectric ceramics with a large piezoelectric anisotropy," *J. Phys. D: Appl. Phys.*, **30**, 1541-1549, (1997).
- 25 M. J. Haun, E. Furman, S. J. Jang, H. A. McKinstry, and L. E. Cross, "Thermodynamics theory of  $\text{PbTiO}_3$ ," *J. Appl. Phys.*, **62**, 3331-3338, 1987.
- 26 D. Damjanovic, T. R. Gururaja, and L. E. Cross, "Anisotropy in piezoelectric properties of modified lead titanate ceramics," *Am. Ceram. Soc. Bull.*, **66**, 699-703, (1987).
- 27 J. Ricote, C. Alemany, L. Pardo, and C. E. Millar, "Microstructure-properties relationships in samarium modified lead titanate piezoceramics\_II. Dielectric, piezoelectric, and mechanical properties," *Acta mater.*, **44**, 1169-1179, (1996).
- 28 C. M. Foster, G.-R. Bai, R. Csencsits, J. Vetrone, R. Jammy, L. A. Wills, E. Carr, and J. Amano, "Single-crystal  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  thin films prepared by metal-organic chemical vapor deposition: Systematic compositional variation of electronic and optical properties," *J. Appl. Phys.*, **81**, 2349-2357, (1997).
- 29 D. V. Taylor, "Dielectric and piezoelectric properties of sol-gel derived  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  thin films," PhD Thesis, Lausanne: Swiss Federal Institute of Technology, 1999.
- 30 X.-H. Du, J. Zheng, U. Belegundu, and K. Uchino, "Crystal orientation dependence of piezoelectric properties of lead zirconate titanate near the morphotropic phase boundary," *Appl. Phys. Lett.*, **72**, 2421-2423, (1998).
- 31 G. H. Haertling, "Chemically reduced PLZT ceramics for ultra-high displacement actuators," *Ferroelectrics*, **154**, 101-106, (1994).
- 32 J.F. Tressler, Q.C. Xu, S. Yoshikawa, K. Uchino and R.E. Newnham, "Composite flextensional transducers for sensing and actuating" *Ferroelectrics* **156**, 67-72 (1994).

